

## CLAIMS

Therefore, at least the following is claimed:

- 1        1.        A membrane, comprising:  
2                    a flexible proton electrolyte membrane having the characteristic of a  
3                    proton conductivity of about  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  S/cm at a temperature range of  
4                    about 30°C to about 180°C and a relative humidity of about 0% to 100%.
  
- 1        2.        A fuel cell, comprising:  
2                    a flexible proton electrolyte membrane having the characteristic of a  
3                    proton conductivity of about  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  S/cm at a temperature range of  
4                    about 30°C to about 180°C and a relative humidity of about 0% to 100%; with the  
5                    proviso that the fuel cell does not include a humidifier, a catalyst, and a thermal  
6                    management system for controlling the temperature in the fuel cell.
  
- 1        3.        A flexible proton electrolyte membrane, comprising:  
2                    a hybrid inorganic-organic copolymer network having at least one  
3                    backbone unit having a formula  $[-O-Si(WX)-O-Si(YZ)-R^1-]$ , wherein each of W,  
4                    X, Y, and Z is selected from  $-OPO_3H_2$ ,  $-R^2A$ ,  $-R^3$ ,  $-O-$ , and  $-OPO_3H_2$ , and  
5                    wherein  $R^1$ ,  $R^2$ , and  $R^3$  are each hydrocarbons.

- 1        4.        The membrane of claim 3, wherein  $R^1$  is selected from a linear  $C_2$  to  $C_{20}$

2               hydrocarbon, a branched  $C_2$  to  $C_{20}$  hydrocarbon, a halogen-substituted linear  $C_2$  to

3                $C_{20}$  hydrocarbon, and a halogen-substituted branched  $C_2$  to  $C_{20}$  hydrocarbon.
- 1        5.        The membrane of claim 3, wherein  $R^2$  is selected from a linear  $C_2$  to  $C_{20}$

2               hydrocarbon, a branched  $C_2$  to  $C_{20}$  hydrocarbon, a hydrocarbon including an

3               aromatic ring, a halogen-substituted linear  $C_2$  to  $C_{20}$  hydrocarbon, a halogen-

4               substituted branched  $C_2$  to  $C_{20}$  hydrocarbon, and a halogen-substituted

5               hydrocarbon including an aromatic ring.
- 1        6.        The membrane of claim 3, wherein  $R^3$  is selected from  $CH_3$  and  $C_2H_5$ .
- 1        7.        The membrane of claim 3, wherein A is selected from  $-SO_3H$ ,  $SO_2NHSO_2CF_3$ ,

2                $-CF_2SO_3H$ , and  $-CF_2SO_2NHSO_2CF_3$ .
- 1        8.        The membrane of claim 3, wherein the backbone unit is crosslinked with a second

2               backbone unit.
- 1        9.        The membrane of claim 3, wherein each of W, X, Y, and Z are different.
- 1        10.       The membrane of claim 3, wherein the backbone unit has a formula

2                $[-O-Si(WX)-O-Si(YZ)-R^1-O-R^4]$ , wherein each of W, X, Y, and Z is selected

3               from,  $-R^2A$ ,  $-R^3$ ,  $-O-$ , and  $-OPO_3H_2$ , wherein  $R^4$  is a hydrocarbon.

- 1        11.    The membrane of claim 10, wherein  $R^4$  is selected from a linear  $C_2$  to  $C_{20}$   
2               hydrocarbon, a branched  $C_2$  to  $C_{20}$  hydrocarbon, a halogen-substituted linear  $C_2$  to  
3                $C_{20}$  hydrocarbon, and a halogen-substituted branched  $C_2$  to  $C_{20}$  hydrocarbon.
- 1        12.    The membrane of claim 3, wherein the backbone unit has a formula  
2                $[-O-Si(WX)-O-Si(YQ)-R^1-Si(YQ)-]$ , wherein each of W, X, and Y is selected  
3               from  $-OPO_3H_2$ ,  $-R^2A$ ,  $-R^3$ ,  $-OPO_3H_2$ , wherein Q includes  $-O-Si-R^8-Si-$  wherein  $R^2$   
4               and  $R^3$  are each hydrocarbons, wherein each of  $R^1$  and  $R^8$  are selected from a short  
5               chain hydrocarbon and a long chain hydrocarbon, wherein  $R^1$  and  $R^8$  are different,  
6               wherein the short chain hydrocarbon is selected from a linear  $C_2$  to  $C_{20}$   
7               hydrocarbon, a branched  $C_2$  to  $C_{20}$  hydrocarbon, a halogen-substituted linear  $C_2$  to  
8                $C_{20}$  hydrocarbon, and a halogen-substituted branched  $C_2$  to  $C_{20}$  hydrocarbon, and  
9               wherein a long chain hydrocarbon is selected from a hydrocarbon having a  
10              molecular weight from about 500 to 100,000 and a halogen-substituted  
11              hydrocarbon having a molecular weight from about 500 to 100,000.
- 1        13.    The membrane of claim 3, wherein the membrane is incorporated in a fuel cell.

- 1        14.    A membrane formed from mixing components comprising:  
 2                    at least one hybrid inorganic-organic copolymer network former  
 3        compound;  
 4                    a first compound including an inorganic acid group;  
 5                    a Si-O-Si inorganic backbone former compound; and  
 6                    a H<sub>3</sub>PO<sub>4</sub> compound.
- 1        15.    The membrane of claim 14, wherein the inorganic acid group is selected from  
 2                    -SO<sub>3</sub>H, -SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub>, -CF<sub>2</sub>SO<sub>3</sub>H, and -CF<sub>2</sub>SO<sub>2</sub>NHSO<sub>2</sub>CF<sub>3</sub>.
- 1        16.    The membrane of claim 14, wherein the hybrid inorganic-organic copolymer  
 2                    network former compound includes an epoxide ring containing alkoxysilane  
 3        compound.
- 1        17.    The membrane of claim 16, wherein the epoxide ring containing alkoxysilane  
 2                    compound is selected from an aliphatic epoxide ring containing alkoxysilane  
 3                    compound and a cycloaliphatic epoxide ring containing alkoxysilane compound.
- 1        18.    The membrane of claim 17, wherein the epoxide ring containing alkoxysilane  
 2                    compound is selected from (D<sub>3-x</sub>M<sub>x</sub>)SiR<sup>5</sup>C<sub>2</sub>H<sub>3</sub>O and (D<sub>3-x</sub>M<sub>x</sub>)SiR<sup>5</sup>C<sub>6</sub>H<sub>9</sub>O, wherein  
 3                    D can be selected from C<sub>2</sub>H<sub>5</sub>O and CH<sub>3</sub>O, M is selected from C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>, R<sup>5</sup> is  
 4                    a C<sub>2</sub> to C<sub>20</sub> hydrocarbon chain, and x is from 0 to 2.

- 1        19.    The membrane of claim 17, wherein the epoxide ring containing alkoxysilane  
2                compound is selected from (3-glycidoxypropyl)methyldiethoxysilane, (3-  
3                glycidoxypropyl)methyldimethoxysilane, (3-glycidoxypropyl)triethoxysilane, (3-  
4                glycidoxypropyl)trimethoxysilane, 5,6-epoxyhexyltriethoxysilane, 5,6-  
5                epoxyhexyltrimethoxysilane, 2-(3,4-epoxycyclohexyl)ethyltriethoxysilane, and 2-  
6                (3,4-epoxycyclohexyl)ethyltrimethoxysilane.
- 1        20.    The membrane of claim 14, wherein the hybrid inorganic-organic copolymer  
2                network former is selected from an aliphatic diepoxide monomer and a  
3                cycloaliphatic diepoxide monomer.
- 1        21.    The membrane of claim 20, wherein the hybrid inorganic-organic copolymer  
2                network former is selected from  $(\text{C}_2\text{H}_3\text{O})\text{R}^6(\text{C}_2\text{H}_3\text{O})$  and  $\text{C}_6\text{H}_9\text{OR}^6\text{C}_6\text{H}_9\text{O}$ ,  
3                wherein R is a  $\text{C}_2$  to  $\text{C}_{20}$  hydrocarbon chain.
- 1        22.    The membrane of claim 20, wherein the hybrid inorganic-organic copolymer  
2                network former is selected from 1,3-butadiene diepoxide, dicyclopentadiene  
3                diepoxide, and 3,4-epoxycyclohexylmethyl-3,4,-epoxy-cyclohexanecarboxylate.

- 1        23.    The membrane of claim 14, wherein first compound including an inorganic acid  
2                    group includes  $(D_{3-x}M_x)SiR^7A$ , wherein D can be selected from  $C_2H_5O$  and  $CH_3O$ ,  
3                    M is selected from  $C_2H_5$  and  $CH_3$ ,  $R^7$  is a  $C_2$  to  $C_{20}$  hydrocarbon chain, x is from 0  
4                    to 2, and wherein A is an inorganic acid group is selected from  $-SO_3H$ , -  
5                     $SO_2NHSO_2CF_3$ ,  $-CF_2SO_3H$ , and  $-CF_2SO_2NHSO_2CF_3$ .
- 1        24.    The membrane of claim 14, wherein the first compound including an inorganic  
2                    acid group is selected from sulfonated phenyltriethoxysilane (SPS), sulfonated  
3                    phenylethyltriethoxysilane, and 3-(trihydroxysilyl)-1-propane sulfonic acid.
- 1        25.    The membrane of claim 14, wherein the Si-O-Si inorganic backbone former  
2                    compound is selected from tetraethoxysilane and tetramethoxysilane.
- 1        26.    The membrane of claim 14, wherein the hybrid inorganic-organic copolymer  
2                    network former compound is from about 20 to 80 mole ratio of the membrane, the  
3                    first compound including an inorganic acid functional group is from about 0 to 20  
4                    mole ratio of the membrane, the Si-O-Si inorganic backbone former compound is  
5                    from about 20 to 80 mole ratio of the membrane, and the  $H_3PO_4$  compound is  
6                    about 0.1 to 1.5 times the total Si moles in the membrane.

- 1        27.    A membrane formed from mixing components comprising:
- 2                    a bis(alkylalkoxysilyl)-terminated polymer compound;
- 3                    a bis(trialkoxysilyl)-terminated short organic chain compound;
- 4                    a first compound including an inorganic acid group;
- 5                    a Si-O-Si inorganic backbone former compound; and
- 6                    a H<sub>3</sub>PO<sub>4</sub> compound.
- 1        28.    The membrane of claim 27, further comprising a heterocycle compound.
- 1        29.    The membrane of claim 28, wherein the imidazole-ring containing compound is
- 2                    selected from imidazole, benzimidazole, 2-phenyl imidazole (PI), 2-methyl 4-
- 3                    ethyl imidazole, and imidazole-2-carboxaldehyde.
- 1        30.    The membrane of claim 27, wherein the bis(alkylalkoxysilyl)-terminated polymer
- 2                    compound includes (D<sub>3-x</sub>M<sub>x</sub>)SiR<sup>9</sup>Si (D<sub>3-x</sub>M<sub>x</sub>), wherein D can be selected from
- 3                    C<sub>2</sub>H<sub>5</sub>O and CH<sub>3</sub>O, M is selected from C<sub>2</sub>H<sub>5</sub> and CH<sub>3</sub>, R<sup>9</sup> is a linear C<sub>2</sub> to C<sub>20</sub>
- 4                    hydrocarbon chain, and x is from 1 to 2.

1        31.    The membrane of claim 30, wherein the bis(alkylalkoxysilyl)-terminated polymer  
 2                compound is selected from bis((3-methyldimethoxysilyl)propyl)polypropylene  
 3                oxide, bis((3-methyldimethoxysilyl)propyl)polytetraethylene oxide,  
 4                bis(methyldimethoxysilyl)poly(1-butene), bis(methyldimethoxysilyl)polyethylene,  
 5                bis(dimethylmethoxysilyl)polyethylene, bis(methyldimethoxysilyl)polypropylene,  
 6                bis(methyldimethoxysilyl)polyvinylidene fluoride,  
 7                bis(methyldimethoxysilyl)polystyrene,  
 8                bis(methyldimethoxysilyl)polytetrafluoroethylene,  
 9                bis(methyldimethoxysilyl)polyvinyl chloride, and  
 10              bis(methyldimethoxysilyl)polyvinyl alcohol.

1        32.    The membrane of claim 27, wherein the bis(trialkoxysilyl)-terminated short organic  
 2                chain compound includes  $(D_3)SiR^{10}Si(D_3)$ , wherein D can be selected from  $C_2H_5O$   
 3                and  $CH_3O$ ,  $R^{10}$  is a linear  $C_2$  to  $C_{20}$  hydrocarbon chain, and x is from 1 to 2.

1        33.    The membrane of claim 32, wherein the bis(alkylalkoxysilyl)-terminated polymer  
 2                compound is selected from bis(triethoxysilyl)ethane, bis(triethoxysilyl)octane,  
 3                bis(triethoxysilyl)nonane, bis(triethoxysilyl)methane,  
 4                bis(triethoxysilylethyl)benzene, bis(triethoxysilyl)hexane,  
 5                bis(trimethoxysilylpropyl)amine, bis[(trimethoxysilyl)propyl]ethylenediamine,  
 6                bis(trimethoxysilyl)ethane, bis(trimethoxysilyl)octane, bis(trimethoxysilyl)nonane,  
 7                bis(trimethoxysilyl)methane, bis(trimethoxysilylethyl)benzene, and  
 8                bis(trimethoxysilyl)hexane.



- 1        34.    The membrane of claim 27, wherein the first compound including an inorganic acid  
2                   group includes  $(D_{3-x}M_x)SiR^{11}A$ , wherein D can be selected from  $C_2H_5O$  and  $CH_3O$ ,  
3                   M is selected from  $C_2H_5$  and  $CH_3$ ,  $R^{11}$  is a  $C_2$  to  $C_{20}$  hydrocarbon chain, x is from 0  
4                   to 2, and wherein A is an inorganic acid group is selected from  $-SO_3H$ , -  
5                    $SO_2NH SO_2CF_3$ ,  $-CF_2SO_3H$ , and  $-CF_2SO_2NH SO_2CF_3$ .
- 1        35.    The membrane of claim 27, wherein the first compound including an inorganic acid  
2                   group is selected from sulfonated phenyltriethoxysilane (SPS), sulfonated  
3                   phenylethyltriethoxysilane, and 3-(trihydroxysilyl)-1-propane sulfonic acid.
- 1        36.    The membrane of claim 27, wherein the Si-O-Si inorganic backbone former  
2                   compound is selected from tetraethoxysilane and tetramethoxysilane.

1        37.     The membrane of claim 27, wherein the membrane includes about 1 to 2 moles of  
2               Si derived from the bis(alkylalkoxysilyl)-terminated polymer compound, about 0 to  
3               3 moles of Si derived from the bis(trialkoxysilyl)-terminated short organic chain  
4               compound, about 0 to 3 moles of Si derived from the first compound including an  
5               inorganic acid group, about 0 to 2 moles of Si derived from the Si-O-Si inorganic  
6               backbone former compound, and wherein about 10% to 150% of the moles of Si  
7               from the bis(alkylalkoxysilyl)-terminated polymer compound, bis(trialkoxysilyl)-  
8               terminated short organic chain compound, the first compound including an  
9               inorganic acid group, the Si-O-Si inorganic backbone former compound, equals  
10              the moles of  $\text{H}_3\text{PO}_4$ .

1        38.     The membrane of claim 28, wherein the membrane includes about 1 to 2 moles of  
2               Si derived from the bis(alkylalkoxysilyl)-terminated polymer compound, about 0 to  
3               3 moles of Si derived from the bis(trialkoxysilyl)-terminated short organic chain  
4               compound, about 0 to 3 moles of Si derived from the first compound including an  
5               inorganic acid group, about 0 to 2 moles of Si derived from the Si-O-Si inorganic  
6               backbone former compound, about 50% to 100% of the moles of Si from the  
7               bis(alkylalkoxysilyl)-terminated polymer compound, bis(trialkoxysilyl)-terminated  
8               short organic chain compound, the first compound including an inorganic acid  
9               group, the Si-O-Si inorganic backbone former compound, equals the moles of  
10               $\text{H}_3\text{PO}_4$ , and about 0% to 50% of the moles of  $\text{H}_3\text{PO}_4$  equals the moles of the  
11              heterocycle compound.

1        39.     A method of preparing a membrane comprising:

2                providing a sol mixture, wherein the sol mixture is from formed by mixing  
3        compounds selected from group 1 or group 2, wherein group 1 comprises at least  
4        one hybrid inorganic-organic copolymer network former compound, a first  
5        compound including an inorganic acid group, a Si-O-Si inorganic backbone former  
6        compound, and a  $\text{H}_3\text{PO}_4$  compound, and group 2 comprises a bis(alkylalkoxysilyl)-  
7        terminated polymer compound, a bis(trialkoxysilyl)-terminated short organic chain  
8        compound, a first compound including an inorganic acid group, a Si-O-Si  
9        inorganic backbone former compound, and a  $\text{H}_3\text{PO}_4$  compound;

10               disposing the mixture on a substrate;

11               heating the mixture; and

12               forming a flexible proton electrolyte membrane having the characteristic of  
13        a proton conductivity of about  $1 \times 10^{-6}$  to  $1 \times 10^{-1}$  S/cm at a temperature range of  
14        about 30°C to about 180°C and a relative humidity of about 0% to 100%.